

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> :	A1	(11) International Publication Number: WO 95/28284
B41M 5/00		(43) International Publication Date: 26 October 1995 (26.10.95)

(21) International Application Number: PCT/EP95/01105

(22) International Filing Date: 24 March 1995 (24.03.95)

(30) Priority Data:

P 44 12 817.7 14 April 1994 (14.04.94) DE  
P 44 26 578.6 27 July 1994 (27.07.94) DE

(81) Designated States: CA, JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

*With international search report.*

(71) Applicant (for all designated States except US): RENKER GMBH & CO. KG [DE/DE]; Kreuzauer Strasse 33, D-52355 Düren (DE).

(72) Inventors; and

(75) Inventors/Applicants (for US only): LIEBLER, Ralf [DE/DE]; Bilsteiner Weg 8, D-52372 Kreuzau (DE). KOCH, Peter [DE/DE]; Vorgebirgsstrasse 181, D-50969 Köln (DE).

(74) Agents: STERNAGEL, H.-G. et al.; Sander Aue 30, D-51465 Bergisch Gladbach (DE).

(54) Title: RECORDING MATERIAL

(57) Abstract

The invention relates to a recording material for the inkjet method having a particularly glossy surface, a substrate material having a metal layer on at least one of its surfaces and it being possible for this metal layer additionally to be provided with a protective layer. The material thus obtained carries an ink-accepting layer on one of the following surfaces: 1. on the metal layer, 2. on the protective layer covering the metal layer, 3. on that surface of the substrate material which faces away from the metal layer. When an image is recorded on the ink-accepting layer on a commercial inkjet plotter, particularly interesting reflecting colour effects are obtained, in particular colours such as silver, gold, golden red, etc. being produced, which are not achievable by means of a conventional inkjet recording method.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin'	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

DescriptionRecording Material

The invention relates to an improved recording material to meet the requirements of the inkjet process.

Such recording material are known in principle. They are paper or transparent or dull plastics films. These materials, in particular the plastics films, carry an ink-accepting layer on at least one of their surfaces. These are generally hydrophilic coatings which are applied to the substrate in a thickness of between 2 and 50 µm. Such layers are particularly suitable for accepting the generally aqueous inks.

WO 92/0772 describes the coating of a substrate material with a mixture of a crosslinkable and a liquid-absorbing polymer, a partially permeable network being formed in the layer after complete reaction of the said polymers.

WO 93/0486 discloses an ink-accepting layer which is composed of the following components: (1) a vinylpyrrolidone, (2) a polyester, (3) an alkylene oxide polymer, (4) a polyvinyl alcohol and (5) a polyether. The layer exhibits particularly good acceptance properties for aqueous inks.

EP-A-524 626 describes a recording material having a layer which consists mainly of porous pseudoboehmite. This coating has the advantage of particularly rapid drying of the ink.

The use of coloured inks in addition to black ink has become established in the production of recordings, in particular image recordings. A wide range of colour effects is achievable by suitable mixing of the primary colours cyan, magenta, yellow and black. In some cases (graphics, advertising, labels), particularly glossy, reflecting co-

lour effects are desirable. Such effects are not achievable by means of conventional known recording materials.

It is the object of the invention to provide a recording material for inkjet processes on which particularly glossy recordings and/or colour effects are achievable with conventional inks.

This object is achieved by a recording material for inkjet recordings having a substrate material which has, at least on one of its surfaces, a metal layer which may be additionally covered with a protective coating, and, either on this metal layer or on the protective layer covering the metal layer or, in the case of a transparent substrate material, optionally on the opposite surface of the substrate material, a transparent recording layer whose gloss is over 70% when measured according to DIN 67530 at an angle of 20°, 60° and 85°.

It is usual to measure the gloss at different angles, depending on the gloss. Relatively dull surfaces are usually measured at 85° and more highly glossy surfaces at 20°. The recording material according to the invention has a gloss of more than 70%, preferably of more than 80%, at all conventional measuring angles. A gloss of more than 90% at the measuring angles 60 and 85° and more than 85% at a measuring angle of 20° is very particularly preferred.

The gloss of the recording material is measured on the recording layer according to DIN 67530 using commercial gloss measuring apparatuses, for example by means of an apparatus obtainable under the name "detectometer" from the company Dr. Lange. The measurement is carried out against the standard gloss master (standard A).

To achieve this gloss of the recording material, the transparent substrate material is provided with a smooth

reflecting metal layer on at least one surface by any desired method. Suitable preferred metals are aluminium, zinc, nickel, chromium, copper, gold, silver or the alloys thereof. The application is preferably effected by vapour deposition at reduced pressure or by cathode sputtering over the substrate material arranged in a chamber. The metal layer may also be composed of several individually applied layers in order to obtain the desired thickness. The thickness of the metal layer is preferably 10 nm to 300 nm.

In order to achieve the desired effect of the metal layer on the surface gloss of the recording layer, the substrate material should have as smooth a surface as possible. This can be achieved by means of a coating on a substrate material, for example paper. A particularly suitable transparent substrate material comprises plastics films of thermoplastic polymers, for example polyester films. Transparent papers are also suitable as substrate material.

In order to protect the metal layer from being scratched, it may additionally be provided with a protective layer. Suitable polymers for this purpose are, for example, poly(meth)acrylates, polyvinyl acetates or copolymers thereof.

The transparent recording layer for inks contains a hydrophilic film-forming polymer. Suitable polymers are polyvinyl alcohol (PVA), polyvinylpyrrolidone (PVP), cellulose derivatives, (meth)acrylic acid derivatives, polyvinyl acetate or copolymers thereof and mixtures of such substances. The recording layer may have a thickness of 2 µm to 50 µm.

This transparent recording layer for inks can, according to the invention, be applied to the following surfaces:

1. to the metal layer
2. to the protective layer covering the metal layer
3. in the case of transparent substrate material, optionally to that surface of the substrate material which faces away from the metal layer.

Since the adhesion of the recording layer to the metal layer is not completely sufficient in some cases, embodiments 2 and 3 are preferred.

In the case of embodiment 3, the effect of the metal layer also occurs through the transparent substrate material towards the surface of the recording layer.

**Examples:**

Example 1

A 100 µm thick polyethylene terephthalate film is provided on one side with an about 50 nm thick aluminium layer by vapour deposition at reduced pressure. The other surface of the film is then coated with the following solution:

Coating composition:

85 kg of water

15 kg of polyvinylpyrrolidone (PVP)

This coating solution is applied with the aid of a 0.8 mm wire-wound doctor to that surface of the film which faces away from the metal layer and is then dried for 2 minutes at 160°. The resulting coating weight of this ink-accepting layer is about 9 g/m<sup>2</sup>. The recording of an image on this final layer on a commercial inkjet plotter, for example Canon BJC 800, gives particularly interesting reflecting colour effects, in particular colours such as silver, gold, golden red, etc. being produced, which are not achievable by means of a conventional inkjet recording method.

Example 2:

A 100  $\mu\text{m}$  thick polyethylene terephthalate film is provided with an aluminium layer by vapour deposition in the same manner as in Example 1. The coating solution described in Example 1 is then applied to this aluminium layer in the same manner. Here too, recording of an image gives the same interesting colour effects.

Example 3:

A polyethylene terephthalate film is coated by vapour deposition on one side in the same manner as in Example 1. The following protective coating is then applied to this metal layer:

Coating composition:

75 kg of methyl ethyl ketone

10 kg of propylene glycol methyl ether

15 kg of commercial acrylate polymer (solid)

This coating solution is applied to the metal layer by means of a 0.4 mm wire-wound doctor and then dried for about 2 minutes at 160°C. The resulting coating weight of this second layer is about 1.5 g. The ink-accepting layer is applied to this second layer as described in Example 1. Here too, recording of an image on this final layer on a commercial inkjet plotter gives the same reflecting colour effects.

**Claims**

1. Recording material for the inkjet method having a substrate material which has a metal layer at least on one of its surfaces, it being possible for this metal layer additionally to be covered with a protective coating, and has, either on this metal layer or on the protective layer covering the metal layer or, in the case of transparent substrate material, optionally on the opposite surface of the substrate material, a transparent or slightly dull recording layer, the gloss, measured on the surface of this recording layer, according to DIN 67530 having a value > 70% when measured at an angle of 20°, 60° and 85°.
2. Recording material according to Claim 1, characterized in that the gloss has a value > 80% at an angle of 20°, 60° and 85°.
3. Recording material according to Claim 1, characterized in that the gloss has a value > 90% at an angle of 60 and 85° and a value > 85% at an angle of 20°.
4. Recording material according to any of Claims 1-3, characterized in that the substrate is a plastics film.
5. Recording material according to any of Claims 1-4, characterized in that the metal layer contains aluminium, zinc, copper, nickel, chromium, gold, silver or alloys thereof.
6. Recording material according to any of Claims 1-5, characterized in that the substrate material is a transparent polyester film.
7. Recording material according to any of Claims 1-6, characterized in that the recording material contains a hydrophilic film-forming material.
8. Recording material according to any of Claims 1-7, characterized in that the hydrophilic material consists of PVA, PVP, cellulose derivatives, (meth)acrylic acid derivatives, vinyl acetate, copolymers thereof or a mixture of these substances.
9. Recording material according to any of Claims 1-8, characterized in that the metal layer is additionally

- 7 -

covered with a protective layer.

10. Recording material according to any of Claims 1-9, characterized in that the protective layer is a (meth)acrylate polymer or copolymer.

**INTERNATIONAL SEARCH REPORT**

International Application No PCT/EP 95/01105
---

**A. CLASSIFICATION OF SUBJECT MATTER**  
**IPC 6 B41M5/00**

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
**IPC 6 B41M**

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 483 798 (EASTMAN KODAK COMPANY) 6 May 1992 see page 3, line 7 - line 13; claims 1-3 see page 3, line 31 - page 4, line 20 ---	1-10
X	PATENT ABSTRACTS OF JAPAN vol. 18, no. 274 (M-1611) 25 May 1994 & JP,A,06 048 025 (TOPPAN PRINTING COMPANY LIMITED) 22 February 1994 see abstract ---	1-10
X	PATENT ABSTRACTS OF JAPAN vol. 4, no. 114 (M-026) 15 August 1980 & JP,A,55 071 586 (FUJI PHOTO FILM COMPANY LIMITED) 29 May 1980 see abstract -----	1-10

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

30 June 1995

Date of mailing of the international search report

12.07.95

Name and mailing address of the ISA

European Patent Office, P.B. 5B18 Patentiaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

Bacon, A

*A.S. Bacon*

**INTERNATIONAL SEARCH REPORT**International Application No  
**PCT/EP 95/01105**

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0483798	06-05-92	US-A-	5278576	11-01-94
		CA-A-	2053531	01-05-92
		JP-A-	4265795	21-09-92
		JP-B-	6062016	17-08-94